THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE,

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED,

Armed Services Technical Information Agency

AD

45688

Line Broadening and Dielectric Relaxation in Compressed Gases

Line Broadening and Dielectric Relaxation in Compressed Gases

by

C. S. E. Phillips

Laboratory for Insulation Research
Massachusetts Institute of Technology
Cambridge, Massachusetts

LINE BROADENING AND DIELECTRIC RELAXATION IN COMPRESSED GASES

by

C. S. E. Phillips

Laboratory for Insulation Research
Massachusetts Institute of Technology
Cambridge, Massachusetts

Abstract: A first attempt is made to investigate the transition from resonance to relaxation spectrum by high-pressure research in the microwave region. Equipment has been developed for studying the dielectric constant and loss of gases and liquids in the K-band region up to 1000 atmospheres at temperatures up to 300°C. Measurements on a nearly spherical molecule of strong dipole moment ($CHClF_2$), on a linear molecule of weak dipole moment (N_2O), and on mixtures of $CHClF_2$ with nitrogen are reported and a preliminary discussion of the results is given.

Introduction

In gases, one finds resonance spectra extending from the far ultraviolet into the microwave region. By condensing gases to liquids and solids, the spectral range from microwaves to d. c., previously empty, fills up with relaxation spectra. These spectra are broad and frequently hard to interpret. By observing the transition from gases to liquids with high pressure techniques, much might be learned about the interaction of molecules leading to this change from resonance to relaxation. The Laboratory for Insulation Research is engaged in dielectric spectroscopy over the electric and optical frequency region, where this question of the transition from the gas state to the condensed phases is a key problem in the molecular analysis. This is one reason why the present in-

vestigation was undertaken.

Very little is known in this field theoretically or experimentally. At the one extreme, resonance absorption in gases at pressures up to a few centimeters of mercury is now well understood. At the other extreme, the general behavior in liquids has been a subject for research for many years but the complicated nature of liquid structure has made a detailed molecular interpretation of dielectric relaxation difficult. The second purpose of our research is therefore to investigate how far experiments using the parameter "pressure" as the variable can contribute to a better understanding of dielectric relaxation phenomena.

As far as we are aware, the only other experimental study on dielectric constant and loss to high pressures is that of David, Hamann, and Pearse[1] who measured CH_3F up to 160 atmospheres at a frequency of 1 Mc/sec. A sudden rise of the dielectric loss occurred when the critical density was reached. Above the critical temperature a smooth transition was observed from gas-like to liquid-like behavior.

Experimental Approach

For rotation spectra as well as for dielectric relaxation in liquids, the main range of interest extends from about 10 cm to 0.1 mm wavelength. The present work, intended as a preliminary study of the inherent possibilities of this type of research, has been limited to only one wavelength (1.22 cm). This wavelength was chosen as being short enough to pick up lower rotation lines, while still long enough to allow the use of standard microwave techniques and equipment. The pressure bomb, however, was designed for a possible extension to millimeter waves.

The absorption and dispersion of the gas under test was measured in a

---

1) H. G. David, S. D. Hamann, and J. F. Pearse, J. Chem. Phys. 20, 969 (1952).

resonant cavity, completely enclosed in a pressure bomb (Fig. 1). Microwave energy from a standard klystron passed through a circular waveguide into the bomb via a glass pressure window.[2] The output signal from the resonator passed through a similar pressure window to an intermediate frequency detector. Using a swept local oscillator, an i-f signal is obtained, amplified, and displayed on a cathode ray screen. Within the limits of accuracy, the height of the pip on the oscillograph is proportional to the signal power. The presence of the pressure windows requires the cavity in transmission because measurements outside the bomb would be complicated by reflections at the windows.

Originally the bomb was designed for an H_{01} type cavity with the coupling method used by Bleaney, Loubser and Penrose[3], but this arrangement proved inflexible when adjustments had to be made. Greater accuracy and reliability in the measurements should be attainable with a suitably designed H_{01} system using base coupling. The results described here have been obtained with an H_{11} cavity having a straightforward input and output waveguide. The apparatus is capable of measuring $\epsilon''/\epsilon_o \equiv \kappa''$ from 0.001 to ca. 0.03. An attempt to increase the range towards higher losses by partially filling the H_{11} cavity with Teflon proved unsuccessful because the H_{21} mode interfered. With the H_{01} cavity where side coupling is not used, this could probably be done.

The H_{11} cavity has the serious disadvantage that its mode is degenerate. Any ellipticity of the cavity barrel produces a second resonance which must be eradicated by the proper placing of a crosswire. Unfortunately, our work deals with wide ranges of dielectric constant and the positions of the crosswire and of the coupling holes may be satisfactory at one pressure but not at another. An awkward difficulty is that this disturbance of the resonance curve of the cavity is hard to distinguish from stray resonance caused by the formation of standing

2) T. C. Poulter, Phys. Rev. 40, 860 (1932).

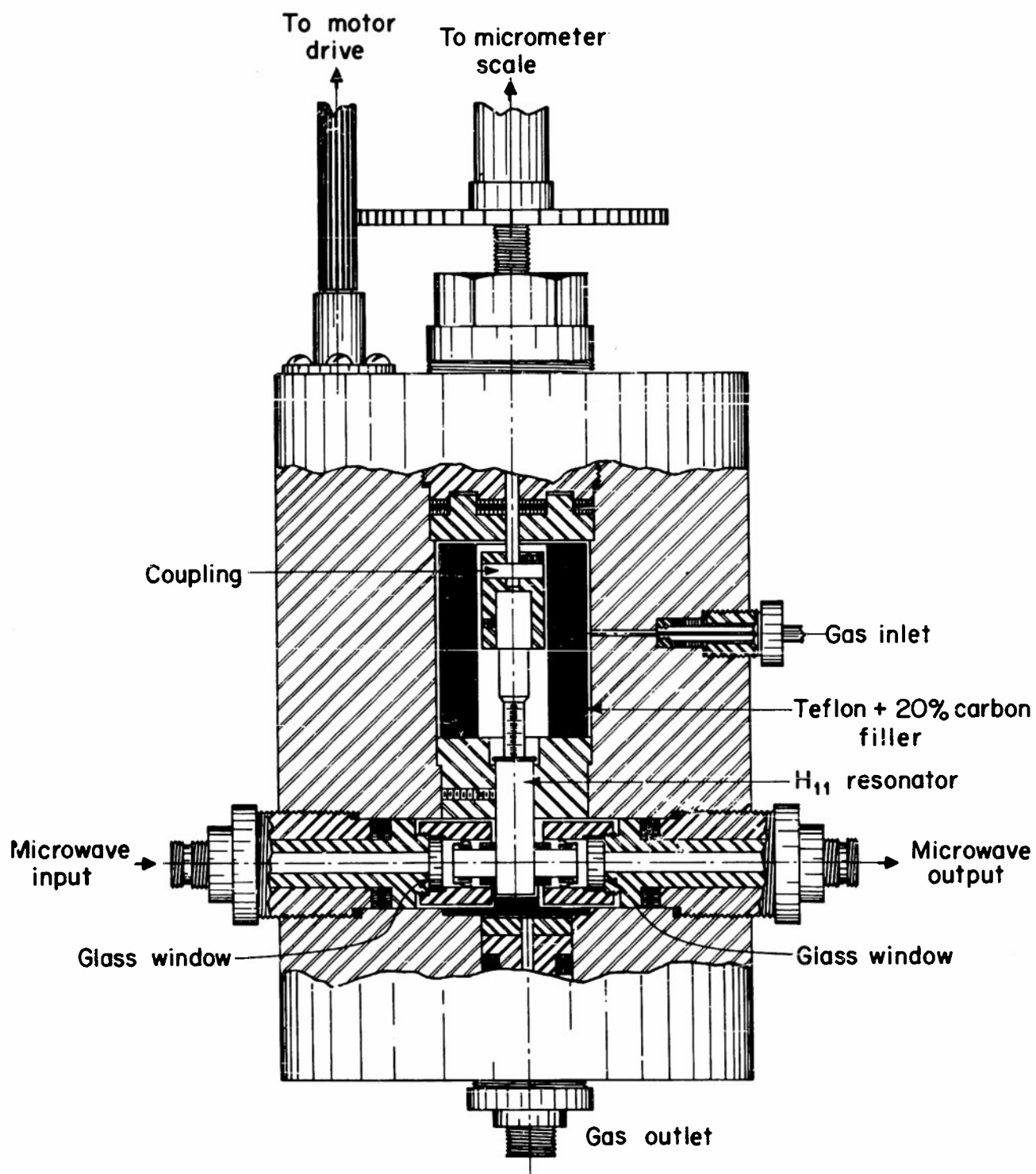3) B. Bleaney, J. H. N. Loubser, and R. P. Penrose, Proc. Phys. Soc. 59, 185 (1947).

Fig. 1.   Microwave absorption pressure bomb.

waves between the windows.

The resonator must be removable from the bomb, but perfectly rigid when inside it; yet, allowance must be made for small strains set up under pressure. The apparatus of Fig. 1 was designed on this basis; any strains were taken up by a sliding action of the windows. (These windows constitute roughly a low Q-tuned circuit since the glass was slightly lossy and the coupling tight.)

Strain on the micrometer had to be avoided. This was accomplished successfully by an Oldham-type coupling which gave "finger touch" motion to the micrometer head. Since it proved to be extremely troublesome to eliminate direct coupling from input to output window, a better arrangement might have been to insert the window rigidly in the base and to let the Oldham coupling absorb the strains which, in any case, proved quite small. Even very efficient screening permits the output windows to pick up from elsewhere than the resonator a tiny signal which may be of the same magnitude as that coming from the cavity when gases of high loss are measured. This leakage was finally eliminated by the simultaneous use of a $\frac{3}{4} \lambda$ folded-back short circuit, beryllium-copper shorting strip, wire wool and absorbent material (carbon impregnated Teflon).

As the micrometer is completely immersed in the gas under test, there is always the possibility of corrosion. The gases and materials for our experiments were chosen with this in mind. Another problem concerns the lubrication of the micrometer spindle. Oil, even silicone oil, will be removed by gases at high pressures. Molybdenum bisulphide powder was used with some success, and the micrometer was frequently removed from the bomb and re-oiled when necessary. Fortunately the gases themselves when compressed, assist in lubrication.

The micrometer was not read directly but connected via the Oldham coupling to a small rod of hardened steel which in turn was joined to a large

diameter rod carrying a second micrometer thread. The latter was cut to the same pitch as the first. Any slight difference in the two threads was taken up by vertical movement in the coupling and the bomb assembled in such a way that the internal micrometer was never forced vertically. In practice, the friction on the small diameter rod proved too great at pressures above 7000 psi. The central Bridgman type seal was therefore replaced, for the experiments at high pressures, by an "O" ring. The resonator was driven by two d-c motors and the micrometer drum and revolution counter read with a telescope.

The bomb was designed for 3000 atm. at temperatures up to $300^{\circ}C$; the maximum pressure used in the experiments here described is 10,000 psi (680 atm.) and the maximum temperature $102^{\circ}C$. The main seals were of silicone rubber and of the Bridgman type. They worked satisfactorily despite the poor mechanical properties of silicone rubber. The unused space within the bomb was filled with absorbent (carbon impregnated Teflon) and the rectangular wave-guide between resonator and windows with ordinary Teflon. The gas outlet, originally intended as the output window of the H_{01} system, served for flushing the bomb and as an alternative point for pressure measurements.

The whole equipment was mounted in a pit in the ground (Fig. 2). Motors, gear mechanism, stirrer, mercury thermoregulator and thermometer were mounted on a removable, heat-insulated platform which also served as the cover of the temperature bath. The silicone-oil bath was heated by two heater coils, one thermostatically and the other manually controlled.

The pressure system is shown in Fig. 3. Pressures up to 10,000 psi were obtained with an ordinary hand pump; a mercury separator prevented contamination of the gas with oil. This separator has a volume of only 50 ml compared with ca. 150 ml for the bomb. For more compressible gases a 400 ml piston-type compressor was used, designed in this laboratory by P. W. Forsbergh, Jr.
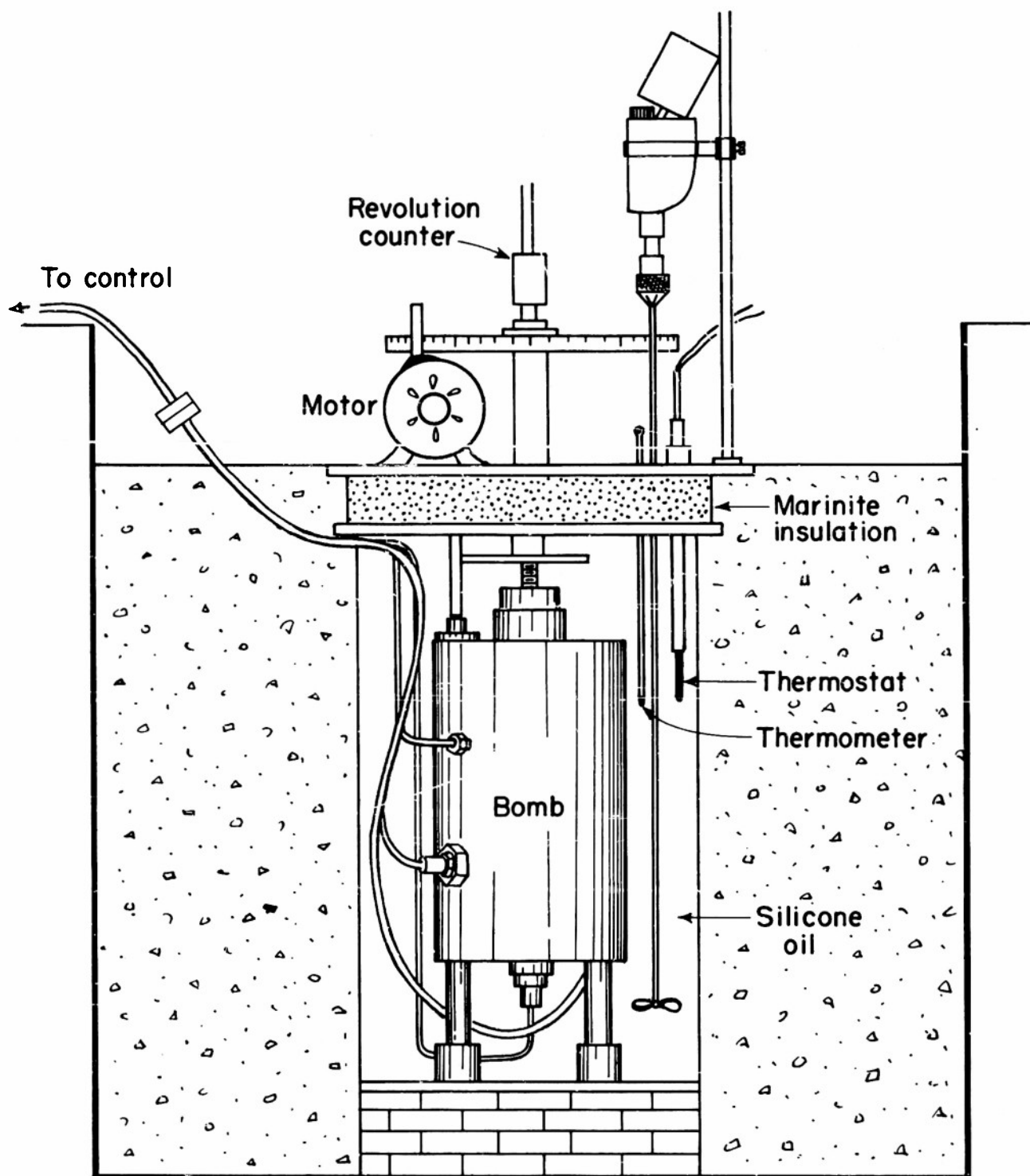
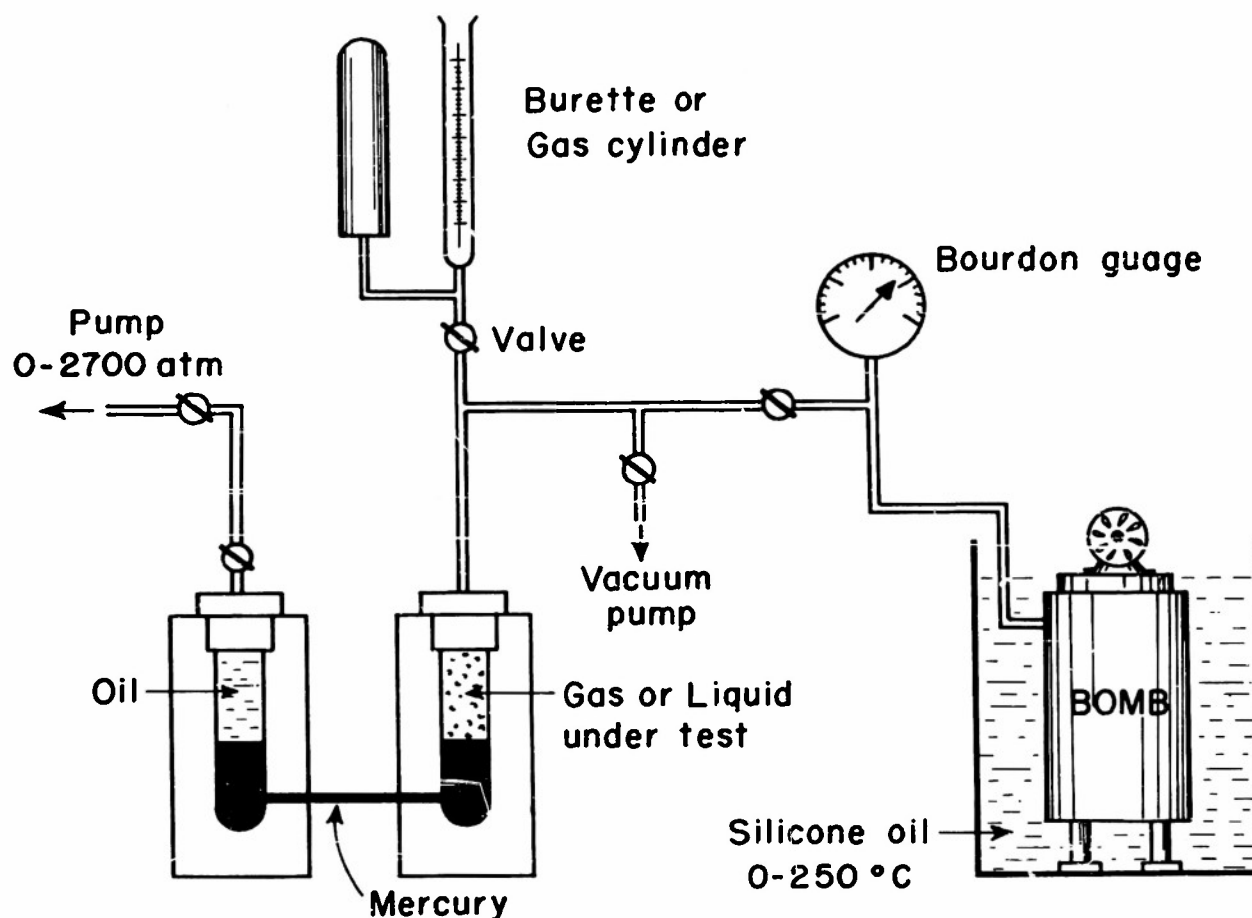Fig. 2   Assembly of microwave absorption apparatus.

Fig. 3. High pressure system (schematic).

Experimental Procedure

After the oil was heated to the desired temperature, allowance was made for the high thermal capacity of the bomb by a waiting period of several hours before measurements were taken. Eventually the results proved not greatly dependent upon temperature and the temperature control was more than sufficient. The whole pressure system was evacuated and then filled with the gas under test. At each pressure, measurements were taken of the resonance position and of the half-power points. The relative dielectric constant κ' and loss factor κ'' were then obtained from the relationships:

$$\kappa' \equiv \epsilon'/\epsilon_0 = 1 + \frac{\lambda^2}{\lambda_{go}^2}\left(\frac{\lambda_{go}^2}{\lambda_{g1}^2} - 1\right)$$

$$\kappa'' \equiv \epsilon''/\epsilon_0 = \frac{2\lambda^2}{n\lambda_{g1}^3}\left[\delta\ell - \delta\ell_0\left\{\frac{1 + n\lambda_{g1}^3/4\ a\lambda_c^2}{1 + n\lambda_{go}^3/4\ a\lambda_c^2}\right\}\right] \quad .$$

Here λ is the free-space wavelength (1.22 cm); λ_c the cut-off wavelength of the H_{11} resonator (1.624 cm); λ_{go} the resonator wavelength in vacuo (1.867 cm); n the number of half wavelengths in the resonator; $\delta\ell$ and $\delta\ell_0$ the distance between half-power points in the gas and in vacuum, respectively. Pressures were measured by Bourdon gauges, previously calibrated against a dead-weight gauge. For gases of a critical temperature above room temperature, the gas cylinder was heated, thereby distilling the gas into the system. For gas mixtures a different procedure was required. The gases, if successively let into the bomb, will not mix properly without stirring. Since a standard amount of the polar component in each mixture was desired, the following method was used. After evacuating the whole system, with the compressor piston fully up, valve D (Fig. 4) was closed to isolate the bomb. Next, the polar gas (here $CHClF_2$) was admitted up to a standard pressure, for example, 55 psi. After closing valve F, nitrogen was admitted to mix by turbulence in the compressor, and the starting pressure of the mixture P_{mix}^0 read on the 0-2000 lb. gauge. After closing valve B, the mixture was pumped into the bomb and measurements were taken at various values of P_{mix}.

As the stored energy of compressed gases can be very large, a liquid was used for initial tests of the pressure equipment. Carbon tetrachloride was selected for this purpose because the molecule is nonpolar, hence no dipole loss is to be expected in the microwave region. However, a small but noticeable loss is observed in this and several other nonpolar liquids. Whiffen[4] has suggested

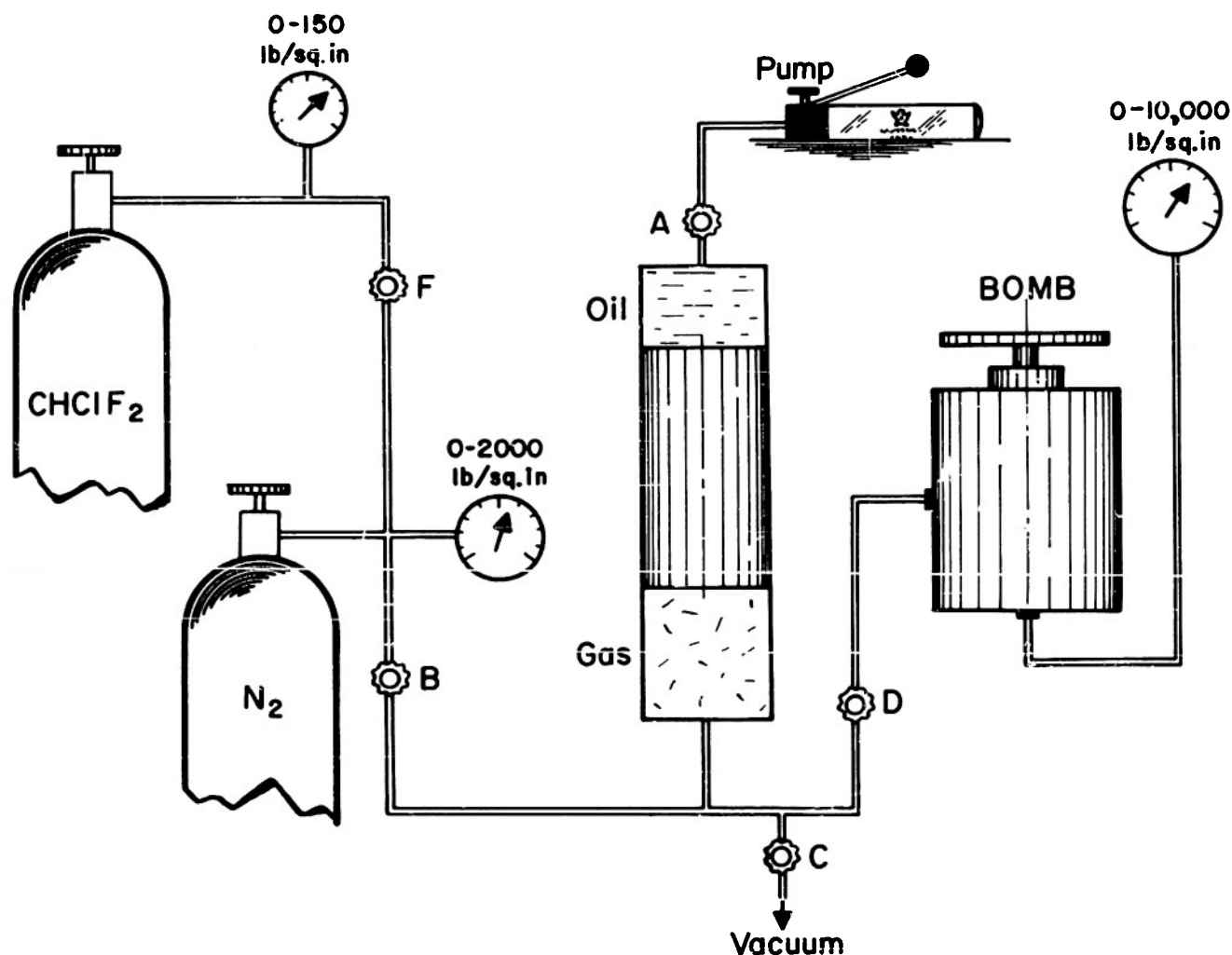4) D. H. Whiffen, Trans. Faraday Soc. <u>46</u>, 124 (1950).

Fig. 4. High-pressure system for gas mixtures.

that this is due to the existence of small semipermanent dipole moments created by the distortion of the chemical bonds as a result of molecular interaction. If such an effect exists it should increase with hydrostatic pressure. At pressures up to 10,000 psi we observed no significant loss increase. However, this may not be surprising as the density change amounts to only ca. 6 percent.

Results

Since no previous measurements of microwave absorption in compressed gases and liquids exist, we decided to study two polar gases of widely different molecular structure: chlorodifluoromethane ($CHClF_2$), a nearly spherical

molecule with a strong dipole moment of 1.396 debye, and nitrous oxide (N_2O), a linear molecule of weak dipole moment (0.166 debye). In addition, we measured some mixtures of chlorodifluoromethane in nitrogen, in analogy to the measurements of polar liquids in non-polar solvents.

The $CHClF_2$, obtained from a commercial cylinder, was measured at three different temperatures up to the highest possible pressures (Fig. 5). A pressure limit was set by excessive losses, which cannot be measured in the microwave cavity. At 17.5° and 40°C this limit was reached by the liquefaction of the gas. Sometimes the gas did not condense on account of supercooling and higher pressures could be reached in the gas phase, as indicated in the 40°C characteristic.

For N_2O[†] the losses were low enough on account of the small dipole moment, that the measurements could be carried into the liquid range (Fig. 6). Below the critical temperature (T_c = 36.5°C), dielectric constant and loss jump abruptly at liquefaction; above this temperature, a smooth transition is observed.

Figure 7 shows the measurements for $CHClF_2$ diluted by N_2 in various concentrations. For very small admixtures of chlorodifluoromethane, the polar molecule interacts essentially only with the nonpolar nitrogen molecules, until condensation sets in.

Discussion

The curves in Figs. 5 to 7 show widely differing shapes and a pronounced temperature dependence. This appearance is partly misleading, since the experimental variable "pressure" has been plotted as abscissa, while the significant variable is the number of molecules per unit volume, N, that is, the density of the gas. Unfortunately, PVT data for polar gases are practically nonexistent in the literature; we hope to measure some density characteristics in the near future.

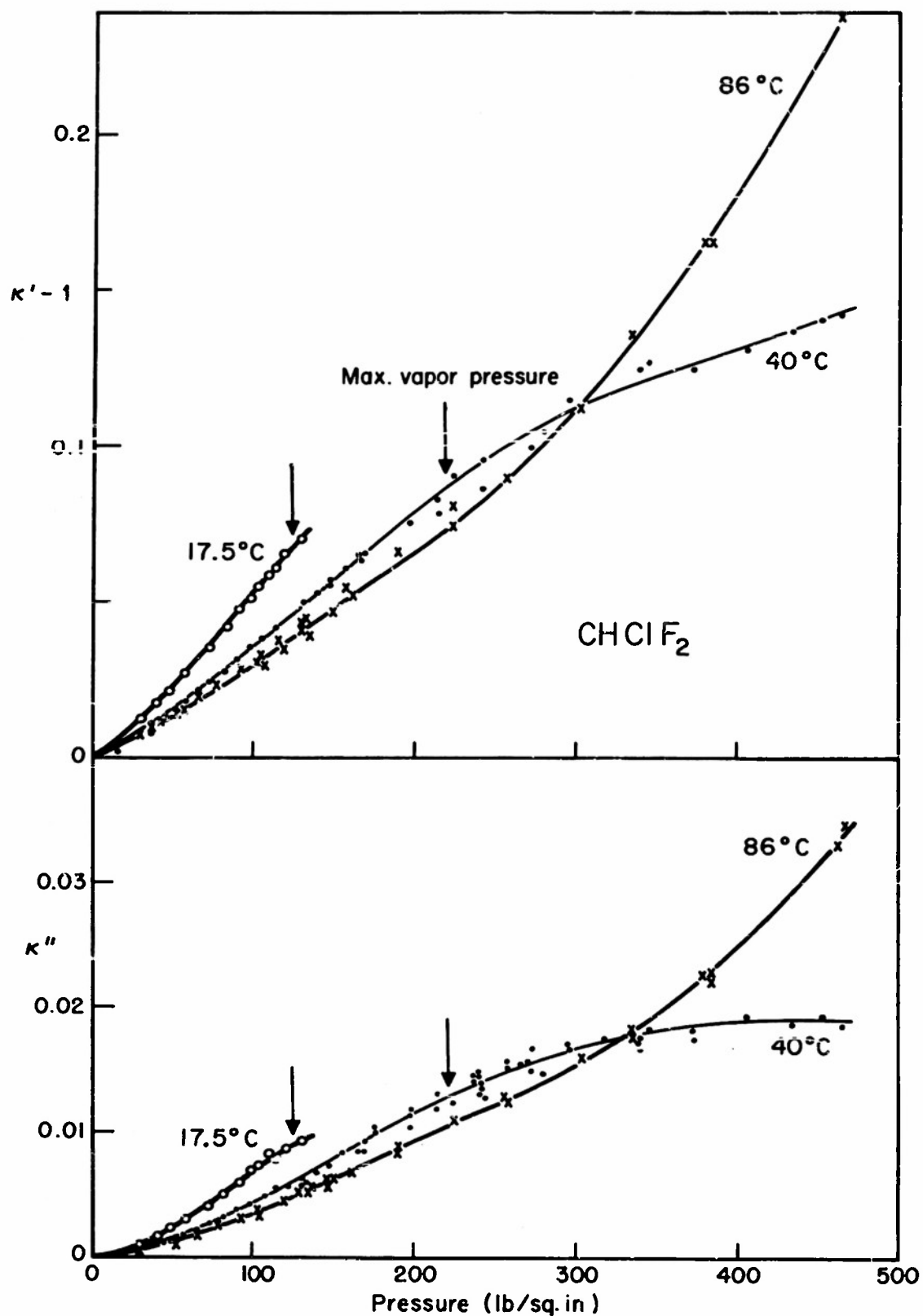[†] Commercial, Mathieson Chemical Corporation, Niagara Falls, N.Y.

Fig. 5. $\kappa' - 1$ and κ'' vs. pressure for chlorodifluoromethane at various temperatures ($\lambda = 1.22$ cm).
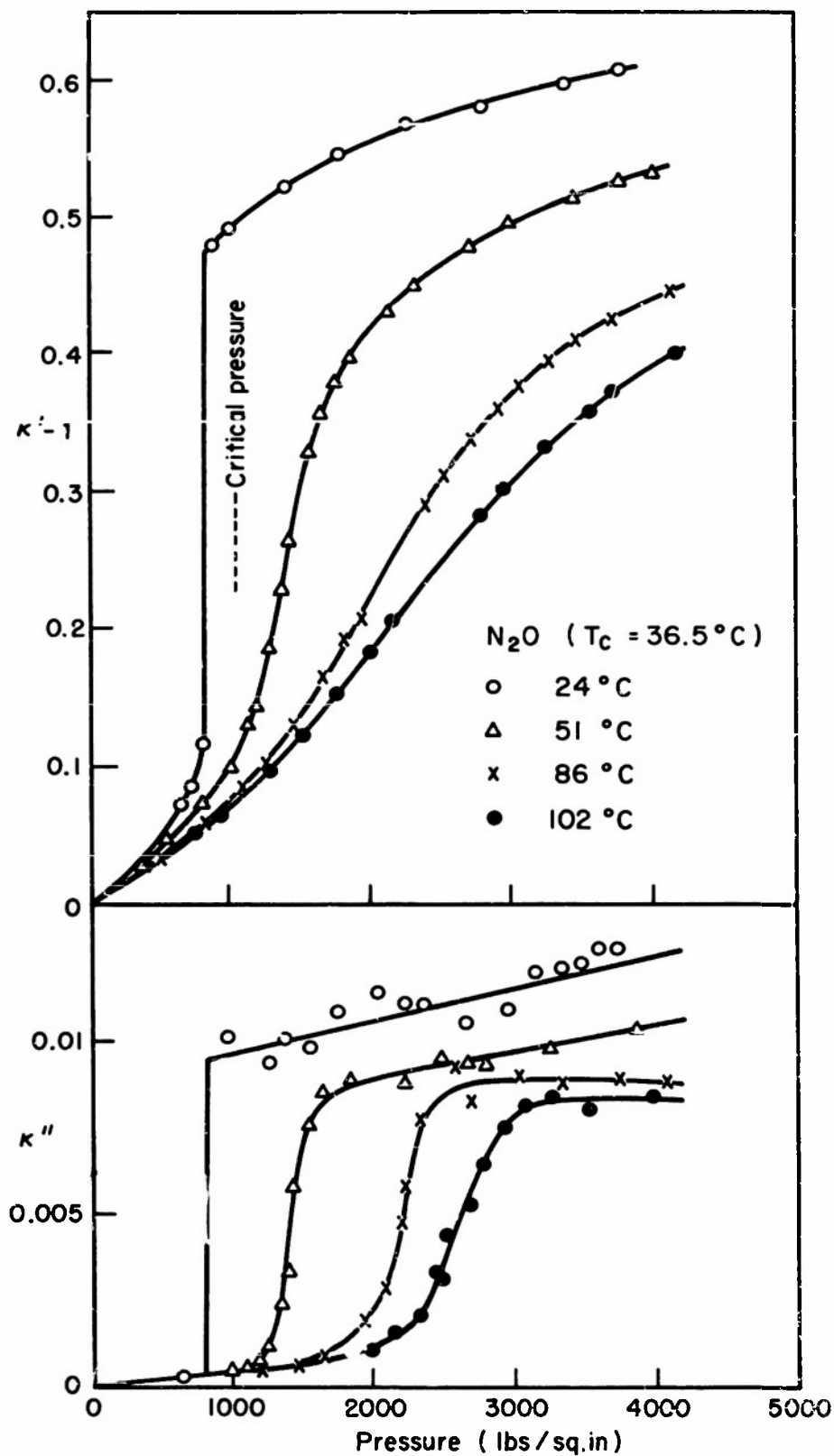
Fig. 6. $\kappa' - 1$ and κ'' vs. pressure for nitrous oxide at various temperatures ($\lambda = 1.22$ cm).
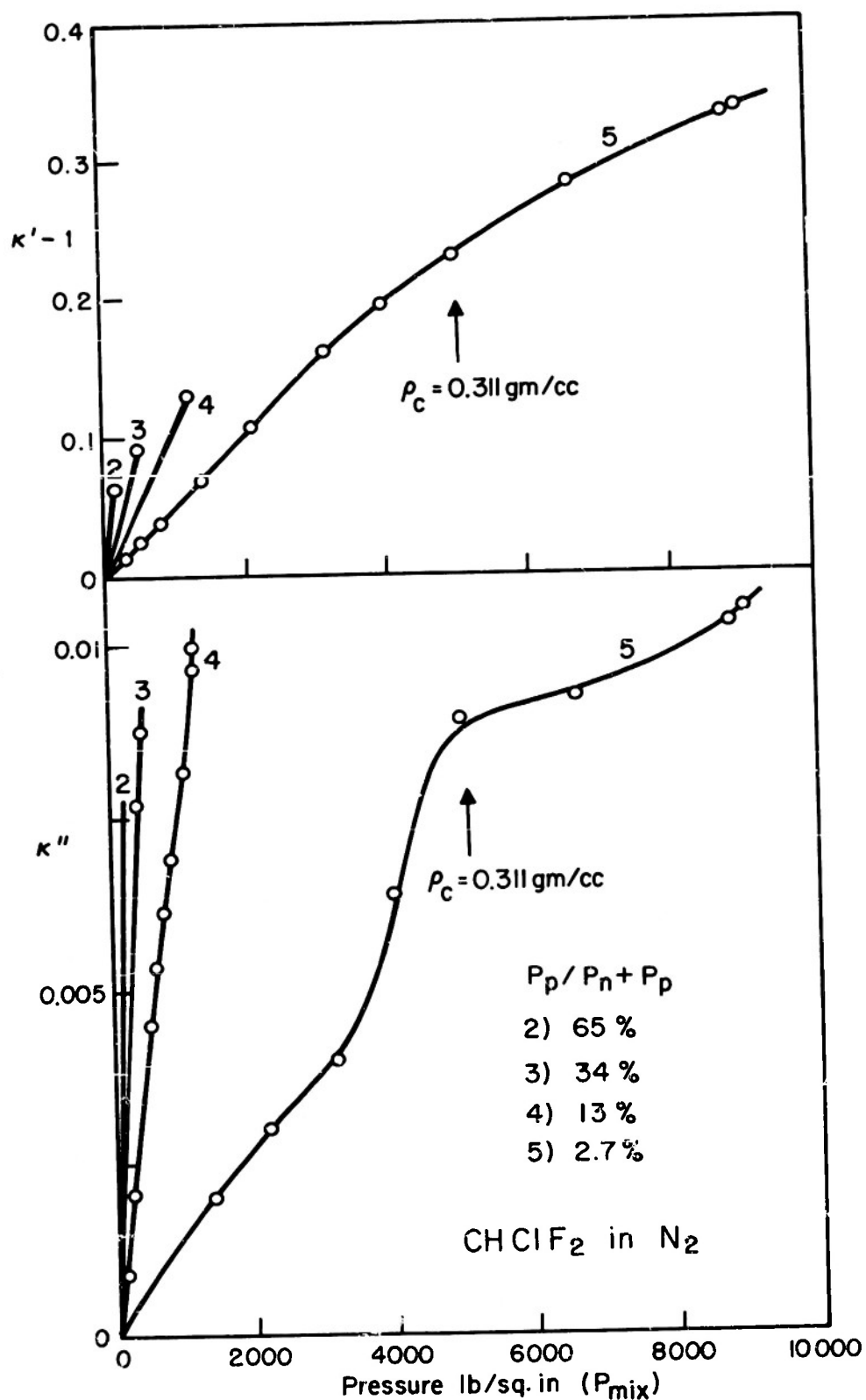
Fig. 7. $\kappa' - 1$ and κ'' vs. pressure for various mixtures of chlorodi-fluoromethane and nitrogen ($\lambda = 1.22$ cm; $T = 24^{\circ}$C).

A way out of this impasse is to remove in a first approximation the factor N by replotting the loss factor κ'' as a function of the electric susceptibility $\kappa' - 1 \equiv X$. The characteristics assume now a much simpler appearance, the parameter temperature is relegated to minor importance, but still the shapes for the three cases differ significantly (Figs. 8 to 10).

To proceed further in our interpretation, we should have recourse to a satisfactory theory of collision broadening, but unfortunately, such a theory does not yet exist.[5] Van Vleck and Weisskopf[6] and also Fröhlich[7] have investigated the problem, originally studied by Lorentz, of the broadening of resonance lines by collisions. Van Vleck and Weisskopf derive a line-shape formula which in the limit of zero resonant frequency transforms into the Debye relaxation equation for polar liquids

$$\kappa' - 1 = \frac{N}{\epsilon_o} \left[(a_e + a_a) + \frac{\mu^2}{3\,kT} \frac{1}{1 + \omega^2 \tau^2} \right]$$

$$\kappa'' = \frac{N}{\epsilon_o} \frac{\mu^2}{3\,kT} \frac{\omega\tau}{1 + \omega^2 \tau^2} \, . \tag{1}$$

However, in this derivation the relaxation time τ has the meaning of an average time interval between collisions and therefore decreases with increasing pressure. The τ of the Debye equation is proportional to a viscosity and increases with pressure, as has been shown, for instance, for the viscosity of glycerin, isobutyl alcohol and eugenol up to 12,000 atmospheres by Danforth.[8] How the theory might be extrapolated from the gaseous to the liquid state, has been discussed by Gross in this laboratory.[9]

5) See A. von Hippel, "Dielectrics and Waves," John Wiley and Sons, New York, 1954, also for this formulation of the equations in the rationalized mks system.

6) J. H. Van Vleck and V. F. Weisskopf, Revs. Mod. Phys. 17, 227 (1945).

7) H. Fröhlich, Nature 157, 478 (1946).

8) W. E. Danforth, Jr., Phys. Rev. 38, 1224 (1931).

9) E. P. Gross, Tech. Rep. 79, Lab. Ins. Res., Mass. Inst. Tech., May, 1954.

Caught in this dilemma, we will attempt a crude interpretation of our data by assuming that they can be represented in a first approximation by the simple relaxation spectrum of Eq. (1). Expressing the loss factor κ'' as function of the susceptibility $\kappa' - 1$ means in this case complete elimination of N, and we obtain

$$\kappa'' = b \, \omega \, \tau \, (\kappa' - 1).$$ (2)

The factor b represents the ratio of orientation polarizability to total polarizability at the frequency ω:

$$b = \frac{\dfrac{\mu^2}{3\,kT} \dfrac{1}{1 + \omega^2 \tau^2}}{a_e + a_a + \dfrac{\mu^2}{3\,kT} \dfrac{1}{1 + \omega^2 \tau^2}} \quad .$$ (3)

Since in our experiments the frequency is kept constant, the situation is relatively simple as long as we find ourselves not directly in the dispersion region, but, for example, appreciably below it ($\omega\tau \ll 1$). Here b is a c nstant, if we can neglect interactions like association, which would change the dipole moment μ and the electronic and atomic polarizabilities a_e and a_a.

Returning to chlorodifluoromethane, we know that its rotational spectrum will consist of many strong resonance lines in the microwave and infrared region and that the absorption already at one atmosphere, as Hershberger[10] measured, consists of the contributions of many lines. In the plot of Fig. 8, the slope of the straight-line portion is $b\omega\tau = 0.14$. To obtain b and τ individually, we can return to Fig. 5 and try the following approximation:

If for $T = 86^\circ C$ the $CHClF_2$ behaves like a perfect gas ($p = NkT$), the loss factor of Eq. (1) can be rewritten

$$\kappa'' = \frac{p\mu^2}{3\,k^2 T^2} \frac{\omega\tau}{1 + \omega^2 \tau^2} \quad .$$ (4)

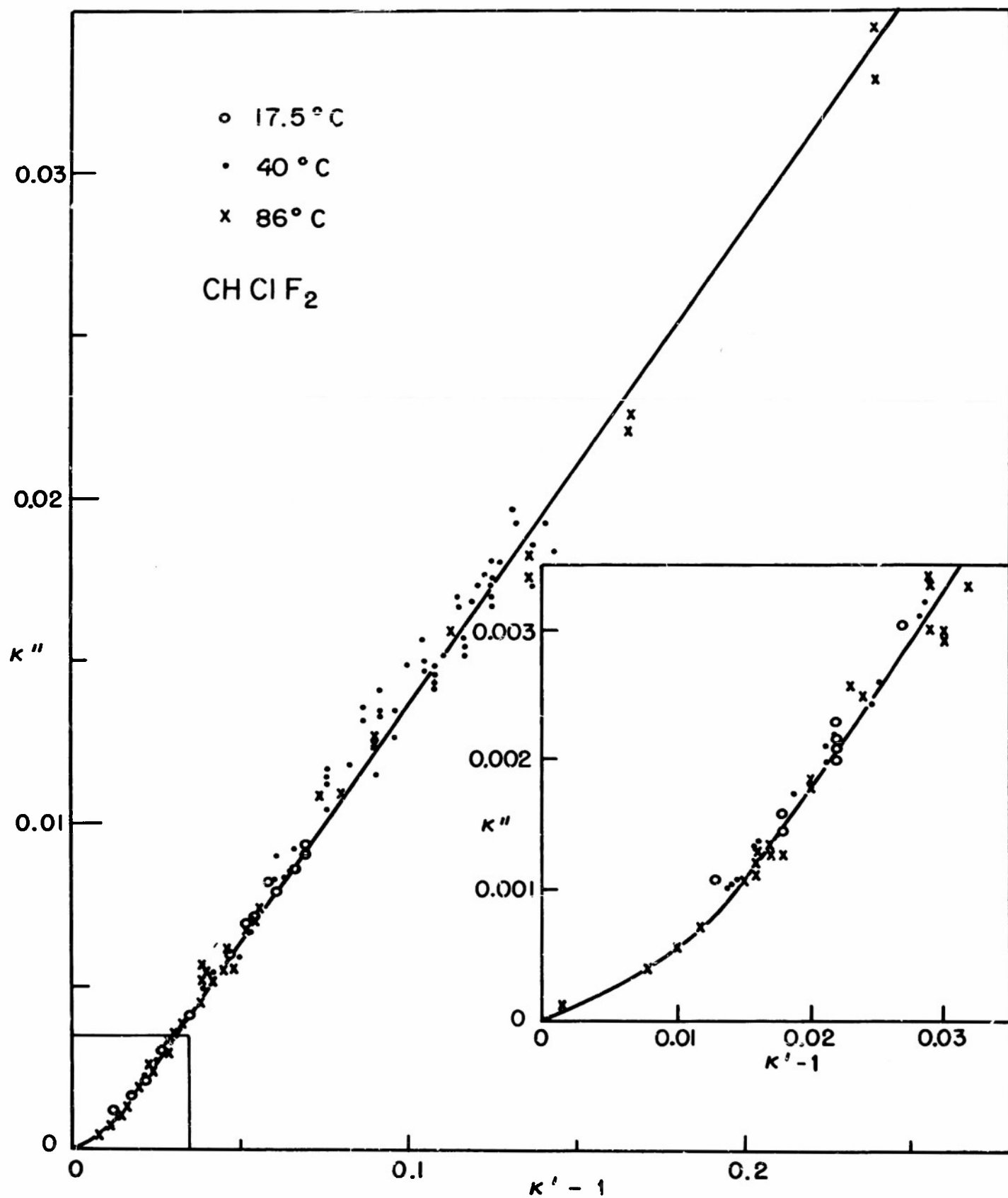10) J. E. Walter and W. D. Hershberger, J. Appl. Phys. 17, 814 (1946).

Fig. 8. κ'' vs. $\kappa' - 1$ for chlorodifluoromethane at various temperatures (λ = 1.22 cm).

For $\mu = 1.396$ D and $\omega\tau = 1$ the maximum loss factor should be

$$\kappa''_{max} \simeq 0.0017 \text{ per atmosphere} \qquad . \qquad (5)$$

Our measured loss factor is about $\kappa'' \simeq 0.0005$ per atmosphere. Since

$$\frac{\kappa''}{\kappa''_{max}} = \frac{2\omega\tau}{1 + \omega^2\tau^2} \qquad , \qquad (6)$$

we find $\omega\tau \simeq 0.15$ and b $\simeq 0.8$.

This result appears quite reasonable. It says that the critical wavelength of the loss maximum lies about at 2 mm; that the major part of the polarization arises from dipole orientation (b near unity); and that the relaxation time $\tau \simeq 10^{-12}$ sec. is, in the linear part of the characteristic, independent of temperature and density within the limits of accuracy of the experiment (ca. 5%). Differently expressed: the free rotation is destroyed by collisions, but the statistical orientation time of the molecules is small as compared to $1/\omega$ and independent of pressure and temperature in the range measured. The deviation from the straight line portion at low pressures may indicate that here the separate resonance lines have not yet fully merged.

For N_2O, the low-pressure rotational spectrum consists of a sequence of weak lines at 12.3, 6.2, 3.1 mm, etc.[11] The wavelength in our experiment practically coincides with the fundamental, but the absorption is too small to be detected with the present resonator. The line-broadening factor Δv has been measured as 0.067 cm^{-1} per atm.[12], hence the second line would not appreciably contribute before 200 psi are reached and even then not be measurable. Hence we are not surprised to find in Fig. 6 that the absorption is about negligible below 1000 psi. A significant loss sets in when the gas liquefies or reaches the

11) R. G. Shulman, B. P. Dailey and C. H. Townes, Phys. Rev. 78, 145 (1950).

12) A. Adel and E. F. Barker, Revs. Mod. Phys. 16, 236 (1944).

density of the liquid (Fig. 9).

The rapid rise of the loss indicates a transition from a gas-like to a liquid-like behavior. For this latter part of the characteristic we may use the relaxation equation (1) with greater confidence. By replacing the number of molecules per unit volume, N, with $\frac{\rho N_o}{M}$, where ρ is the orthobaric density at $24^\circ C$ ($\rho = 0.754$ gm/cc)[13], N_o Avogadro's number and M the molecular weight, we find $\kappa''_{max} = 0.0145$. According to Fig. 6, we measured $\kappa'' = 0.0095$, hence $\omega\tau \simeq 0.37$. The critical wavelength of maximum loss in the liquid state lies consequently for the simple relaxation spectrum at about 4.5 mm, which is in line with the known values of other polar liquids.

If the slope of the dotted line in Fig. 9 is identified with $b\omega\tau$ for the liquid state, we find b = 0.05, that is, for N_2O the dipole polarization is only a small fraction of the total polarization. Since b is so small, it should vary according to Eq. (3) approximately inversely proportional to the temperature. The density range unfortunately is insufficient to check this trend. However, that b is small, can be confirmed by comparing the optical dielectric constant κ'_∞, given as

$$\kappa'_\infty - 1 = (1 - b)(\kappa' - 1) \tag{7}$$

with the square of the index of refraction. From n = 1.193[14] we obtain $n^2 - 1 \simeq$ 0.43 as compared to $\kappa'_\infty - 1 \simeq 0.45$ from Fig. 9 with the small b value.

In studies of the dielectric relaxation spectra of liquids and polymers it has proved useful to dissolve the polar component in nonpolar solvents. At very low concentrations the polar molecule interacts only with nonpolar molecules; the environment can be altered by changing the solvent. Furthermore, the influence of the dipolar interaction can be studied by progressively increasing the concentration of the polar constituent. The dielectric characteristics of mixtures

13) D. Cook, Trans. Faraday Soc. 49, 716 (1953).

14) Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, O., 1953-1954, p. 558.
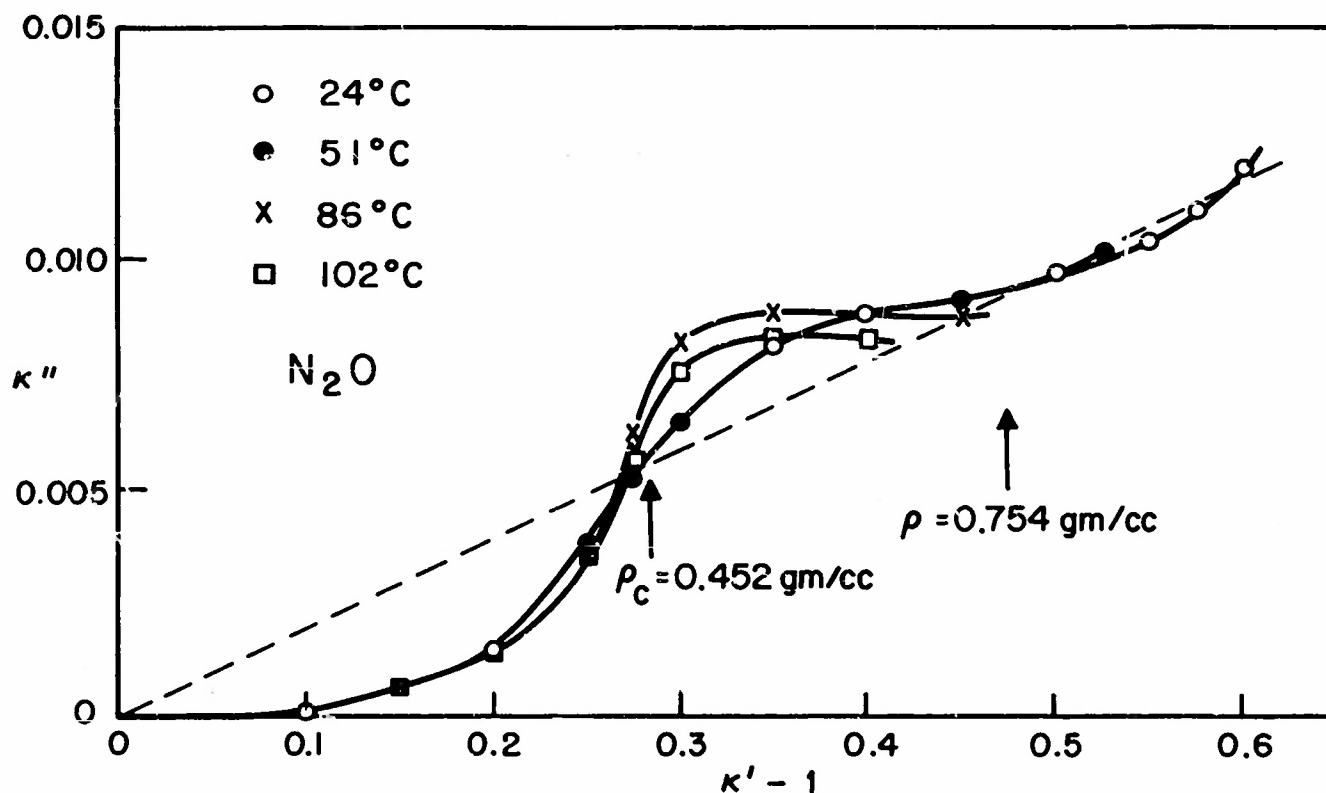
Fig. 9. κ'' vs. $\kappa' - 1$ for nitrous oxide at various temperatures ($\lambda = 1.22$ cm).

of $CHClF_2$ in N_2 (Figs. 7 and 10) are a first installment of this type of measure-ment in the high-pressure gas region.

The initial pressure of the polar component P_p^o was 55 psi; by adding a quantity of nitrogen, the pressure P_{mix}^o is obtained and the ratio P_p^o/P_{mix}^o is called the "concentration". The experimental characteristics show the suscepti-bility and loss factor as function of P_{mix}. Each curve corresponds to a constant ratio of polar to nonpolar molecules, N_p/N_n, which is approximately given as

$$N_p/N_n \simeq \frac{P_p^o}{P_{mix}^o - P_p^o} \qquad . \qquad (8)$$

In addition to the curves of constant concentration, Fig. 10 shows lines of constant N_p obtained as follows: in every original mixture P_{mix}^o is contained the same number of polar molecules per unit volume (equivalent to 55 psi). The
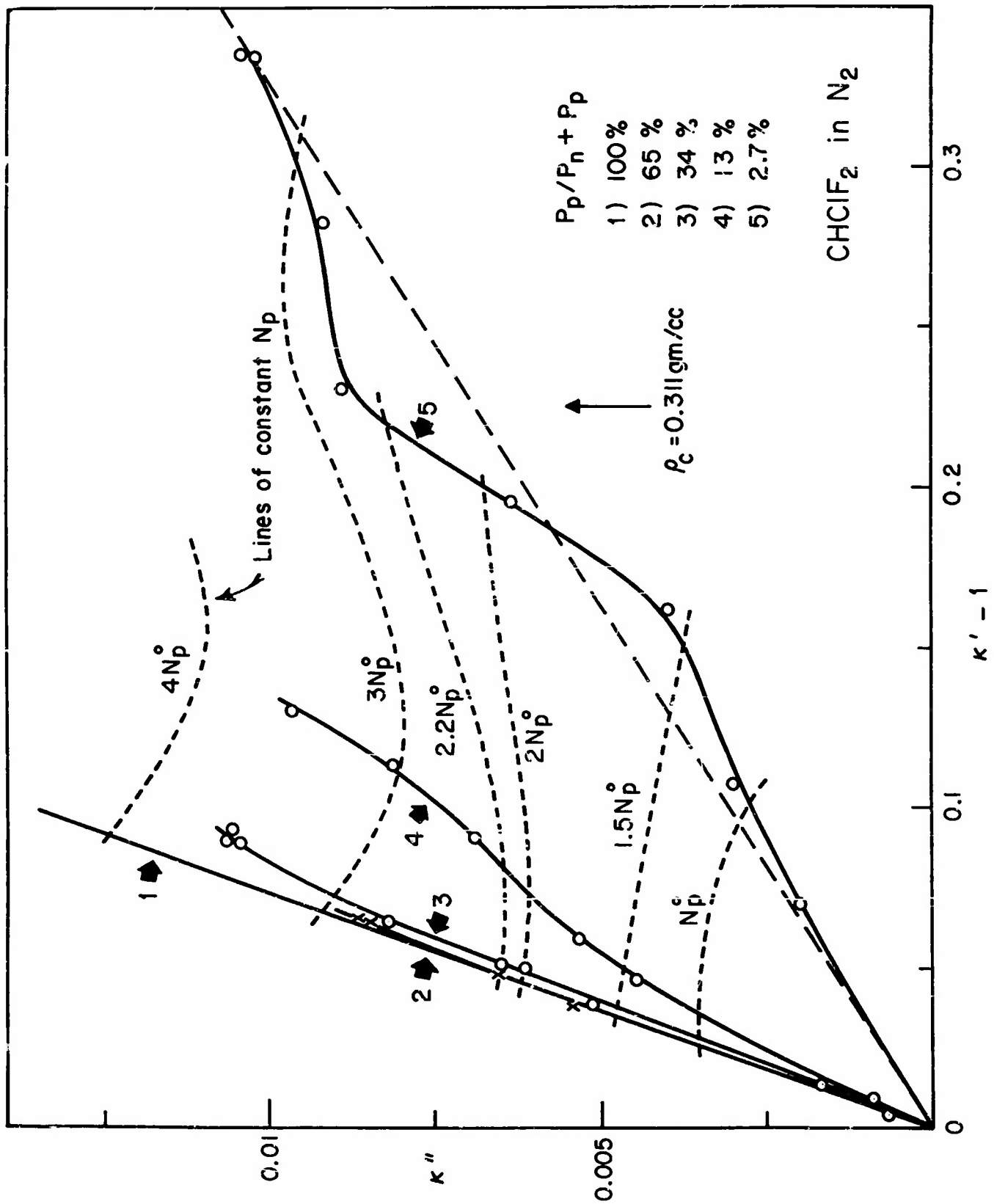
Fig. 10. κ'' vs. $\kappa' - 1$ for various mixtures of chlorodifluoromethane in nitrogen ($\lambda = 1.22$ cm; $T = 24^\circ$C).

susceptibilities of these mixtures are read off in Fig. 7 and translated as the N_p^o curve into Fig. 10. By multiplying the susceptibility values with the corresponding factors 1.5, 2, 2.2, etc., the other curves are drawn.

If the relaxation equation (1) can be applied and the loss expressed as

$$\kappa'' = \frac{\bar{N}_p}{\epsilon_o} \frac{\mu^2}{3\,kT} \frac{\omega\tau}{1 + \omega^2\tau^2} \quad , \tag{9}$$

the curves of constant N_p seem to indicate that the relaxation time of the $CHClF_2$ molecules is first slightly reduced, then increased and reduced again as more and more nitrogen molecules are added. At still higher pressures, τ should increase again as the mixture assumes the properties of a dilute liquid solution.

In the very dilute mixture of 2.7 percent (see Fig. 10) the interaction should practically concern only the individual polar molecules with their nonpolar surroundings, hence τ should be independent of N_p and vary only with N_n. It is interesting to find that this characteristic has a similar S shape as that found for N_2O. In both cases the critical density marks approximately the point of maximum τ. The characteristic finally approaches the slope of the dotted line, represented according to Eq. (2) as $b'\omega\tau = 0.0305$. At this point the loss per polar molecules is about the same as in pure $CHClF_2$, hence $\omega\tau$ is almost unchanged but b', of course, is much smaller than the b of the pure material.

It is obvious that the conclusions here drawn are of a very tentative nature as must be expected from a first foray in an unknown field.

Acknowledgments

Armed Services Technical Information Agency

Because of our limited supply, you are requested to return this copy WHEN IT HAS SERVED YOUR PURPOSE so that it may be made available to other requesters. Your cooperation will be appreciated.

AD 45688

Reproduced by

DOCUMENT SERVICE CENTER
KNOTT BUILDING, DAYTON, 2, OHIO

UNCLASSIFIED